Final Report

3M Brookings South Dakota Ethylene Oxide Petrifilm Abatement Unit Destruction Efficiency Engineering Test

LIMS Project Number: E18-0054

Testing Laboratory

3M Environment, Health, and Safety
EHS Laboratory

3M EHS Laboratory

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Requestor

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The laboratory's quality system has been audited and was found to be in conformance with the EPA GLPs (40 CFR 792) as well as ANSI/ISO/IEC 17025:2005 by an independent assessment. The specific test included in this report is not on the lab's scope of accreditation.

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3M EHS Laboratory – Destruction Efficiency Engineering Test
Report Author: Jess Eldridge
Analytical Team: Jess Eldridge, Kelly Sater

3M Brookings South Dakota Ethylene Oxide Petrifilm Abatement Unit Destruction Efficiency Engineering Test

LIMS Project Number: E18-0054

Date of Report: Date of Last Signature

1 Introduction/Summary

The destruction efficiency (DE) of the ethylene oxide abator at 3M Brookings was evaluated by extractive Fourier Transform Infrared Spectroscopy (FTIR). The inlet and outlet gases of the Petrifilm abatement unit were sampled simultaneously with two MKS FTIR spectrometers measuring the gas phase concentrations of ethylene oxide. Sampling was performed for the duration of 3 runs. Destruction efficiency was determined using inlet & outlet concentrations - averaged over the portion of the run when ethylene oxide was above the limit of quantitation (LOQ) of 0.28 ppmV. Inlet and Outlet airflows were assumed to be equal and as such the DE for this report are solely based on concentration measurements.

Other compounds were seen in the outlet and processed in the data workup but not reported since the object of this report is to evaluate the destruction efficiency of the ethylene oxide. The additional compounds observed in the outlet were carbon monoxide, carbon dioxide, formaldehyde, formic acid, methane, methanol and water. The methane is considered to be the normal atmospheric concentration of approximately 2 ppmV. The presence of CO2 and water is also considered to be primarily from normal atmospheric concentrations with perhaps a slight contribution from the abator operation. Carbon monoxide, formaldehyde, formic acid and methanol are considered byproducts of the abator operation in reducing the ethylene oxide concentration.

The abatement unit was operating at approximately 360 degrees F for Runs 1 and 2. The destruction efficiency was below the 99% DE target or better. As a result the temperature of the abatement unit was increased to 390F for Run 3. The results show that the increased temperature improved the DE to the desired range of >99%. The results show the operating temperature of the abator is a critical factor in demonstrating adequate DE.

A continuous sample slip stream was pumped to the FTIR instruments via 200 feet of heated transfer line; one each from the inlet and outlet of the abator. The instruments were located on the ground level inside the 3M EHS mobile lab positioned near the front employee entrance. The entire sample train was heated; the transfer lines were 121 deg C and the FTIR sample cells were 191 deg C.

The Attest area sterilizer emission data gathering portion of this project was not performed as outlined in the General Project Outline (GPO). Upon site inspection and thorough discussions with resident engineers and operators it was collectively decided not to attempt any in-situ monitoring. Several reasons for this were high concentrations above the LFL likely present in the vent lines and

no adequate ways to physically measure flow. The current system is a batch process without full ventilation of the ductwork between process steps. Three separate sterilizers are plumbed into a common manifold and each operating separately discharging into the vent system. As a result of the meeting the decision was made for the resident engineers and operators to pull together as much information and specifications as possible for the sterilizers and ventilation system. Then to contact a potential abator vendor and meet to discuss design options going forward.

1.1 Destruction Efficiency Results and Discussion

Table 1 Average Ethylene Oxide Concentrations and Destruction Efficiency Results

	Run 1	Run 2	Run 3
Date	1/30/18	1/30/18	1/30/18
Start Time	13:34	15:21	18:25
Conditions	360 F	360F	390F
Inlet Concentrations (ppmV)			
Ethylene Oxide	321	223	331
Outlet Concentrations (ppmV)			
Ethylene Oxide	7.4	4.3	2.5
Ethylene Oxide Destruction Efficiency	97.7%	98.1%	99.2%

2 Methods - Analytical and Preparatory

2.1 Method

Analysis was performed according to a procedure of ETS-8-31.4 “Measurement of Vapor Phase Compounds by Fourier Transform Infrared (FTIR) Spectrometry”, which is based on NIOSH 3800 and EPA Method 320.

The project quality level for this study was designated as “Level Two: Quantitative Monitoring”. Project Quality Level 2 (PQL 2) is appropriate for emission factor estimates and non-compliance test measurements. PQL 2 is appropriate when the project objectives specify the data will not be incorporated in compliance tests of manufacturing emissions, but can be used in certain environmental permitting and regulatory activities such as emission factor estimation.

2.1 Instrumentation

Two FTIR instruments with a 10.2 meter nominal pathlength gas cell were used for the analysis. Table 2 gives sampling and configuration parameters of the instrument(s) used:

Table 2 Instrument Parameters

Instrument Name	9MKS	10MKS
Model	MKS MG2030	MKS MG2030
Date Analyzed	1/30/18	1/30/18
Nominal Pathlength (m)	10.2	10.2
FTIR Cell Temperature (°C)	191	191
Number of Co-added Background Scans	128	128
Number of Co-added Sample Scans	64	64
Scan Range (cm-1)	650–4500	650-4500
Resolution (cm-1)	0.5	0.5

2.2 Calculations

2.2.1 AutoQuant/MG2000 Results

Results generated using the AutoQuant™ (v4.5) or MG2000 (v7.2) software are reported in ppmv (parts per million by volume). The software was used in conjunction with Midac, EPA, PNNL, MKS, and 3M library reference spectra, and manual subtraction of reference spectra in Thermo GRAMS/AI and/or MG2000.

Normally for an emission related project these results are converted to µg using the following equation:

$$\mu g = \frac{Concentration\ (ppm_v) \times Sample\ Gas\ Volume(L) \times Pressure\ (atm) \times Molecular\ Weight\ \left(\frac{g}{mol}\right)}{0.08206(L \times atm \times K^{-1} \times mol^{-1}) \times Cell\ Temperature(K)}$$

However in this case the concentration values were not converted and the DE was based solely on the concentration values. For this engineering test the procedure was considered adequate. It should be noted that a compliance test would be based on emission rates involving air flow measurements at the inlet and outlet locations of the abatement unit.

2.2.2 Manual Subtraction

The concentration of a target analyte in a sample FTIR spectrum was verified using manual subtraction of a reference spectrum from the sample spectrum by means of Thermo GRAMS or MG2000 software. The relative fraction of the reference spectrum, or subtraction factor, is then used to calculate the concentration of the sample in ppmv using the following equation.

$$ppm_v = \frac{subtraction\ factor \times reference\ concentration\ at\ cell\ temp\ (ppm_v \cdot m)}{pathlength\ of\ cell\ (m)}$$

2.2.3 Limit of Quantitation

The limit of quantitation was estimated by manual addition of the analyte quantitative reference spectrum to the sample spectrum. Using the Thermo GRAMS or MG2000 software program, the reference spectrum was added until the analyte signal was approximately two times greater than the surrounding noise. The resulting addition (negative subtraction) factor was used to calculate a ppmv concentration using the equation listed in 2.2.2.

3 Analysis

3.1 Calibration

The instrument was calibrated using a 20 ppmV certified (see Attachment 7.4) standard of ethylene (cylinder # SG9169366BAL). The instrument gas cell pathlength was verified before and after sampling. (see Attachment 7.3)

3.2 Blanks/Leak Checks

Before each sample run, the sample-cell was checked for contaminants using compressed house air and/or house nitrogen. Sample train leak checks were performed before testing. The systems were pumped to below atmospheric pressure and all valves closed. The pressure was monitored over at least 5 minutes. A leak of < 4% total sample volume per sampling time frame is the acceptance criteria. Both systems passed this criteria.

4 Data/Sample Retention

This report and all associated data will be archived and retained according to record retention policy.

5 Conclusion

Matrix spiking was not required for this project. Therefore the uncertainty of the gas phase concentration of the given chemicals as measured using FTIR is +/- 23% and is based on 2 times the standard deviation on the last three years in the ISO 17025 FTIR proficiency testing of 3M EHS Lab FTIR operators.

Results are only valid for the described test conditions.

Establishing proper operating temperature of the abatement unit is a critical factor in demonstrating adequate destruction efficiency. This test as well as past testing shows the temperature of near 400 F renders adequate ethylene oxide destruction efficiency.

When the temperature is near 400 F it is observed the oxidation byproducts also drop in concentration providing overall less emissions.

Winter weather conditions create many testing challenges not otherwise requiring special equipment, precautions and effort. For future reference it is recommended that testing be scheduled during weather conditions above the freezing point of water.

6 Signatures

Digitally signed by Jess S. Eldridge
DN: c=US, st=MN, l=St. Paul, ou=3M Environmental Laboratory - authenticated by LRA, email=jseldridge@mmm.com, o=3M, cn=Jess S. Eldridge
Reason: I am the author of this document
Date: 2018.03.27 09:18:21 -05'00'

Jess Eldridge, Field Analyst

Digitally signed by Brian T. Mader
DN: c=US, st=MN, l=St. Paul, ou=3M Environmental Laboratory - authenticated by LRA, email=bmader@mmm.com, o=3M, cn=Brian T. Mader
Reason: I have reviewed this document
Date: 2018.04.04 13:45:34 -05'00'

Brian Mader, EHS Laboratory Management

7 Attachments

7.1 Sample Collection Data Sheet(s)

Peer Review: E18-0054 – “Brookings Abator Engineering Test”

A representative subset of sample spectra, quantitation method, and supporting information was reviewed by Kelly Sater. Specifically, the following spectral files were reviewed:

Date	Result Sheet	Instrument	Spectrum Number	Compound	Filename	Column Header	MG2000 Result (ppmV)	PR Manual Sub. (ppmV)	PR Difference
1/30/2018	9mks_30Jan2018 Outlet	9mks	77	EtO Outlet	9mks_0077.LAB	Ethylene oxide 150c Outlet	0.29	0.323	-12%
1/30/2018	10mks_30Jan2018 Inlet	10mks	65	EtO Inlet	10mks_0065.LAB	Ethylene Oxide Very Low	449.31	447	1%

Signature: 

Digitally signed by Kelly H. Sater
DN: c=US, st=MN, l=St. Paul, ou=EHS Laboratory, o=3M, cn=Kelly H. Sater, email=ksater@mmm.com
Reason: I have reviewed the data as indicated
Date: 2018.02.27 11:01:45 -06'00'
Adobe Acrobat version: 11.0.23

3 EH&S Opns Environmental Laboratory				Extractive FTIR Sample Collection Data Sheet				Page 1 of 1		
Lab Req. No:	E18-0054	Baro, inHg:		0.00	psia	Signal 4K(cn		Signal 2K(cm^{-1}):		#DIV/0!
Project Name:	Brookings EtO Abatement					Test Loc:	(1) nitrogen	CTS Cyl S.N.:	SG9169366BAL	
Computer ID:	10MKS	FTIR ID:	10MKS			(2)	ethylene	(3)	test	
Operator (s):	JSE/KHS	Date:	1/30/2018			(4)	room air	(5)		
Ref. Method:	ETS-8-031	Quality Level:		(1) Screen		(2) Quantative		(3) Comp	(4) Validation	
Collection Dir:	10MKS_30Jan2018					Meth Nam	E18-0087 Method		Inst. Res(cm^{-1}):	0.5
# Scans, BG/Samp:	128	64	Time/Sample, min:		2.1	1.1	Sampling Interval:	cont	Pathlength, m:	10.2000
Cells: PL,Vol	0.5cm, 0.0006	1cm, 0.0113	5cm, 0.0567	10cm, 0.113	4m, 0.209	10m, 2.13	Tape, 5.7	Parr, 0.636 Tube, ID in., length ft	0.125	30 / 0.0123
Leak Check:	Initial, psia:	0.004	Time:	9:47		Final, psia:	0.005	Time: 9:54	Diff, atm, min:	0.001 / 7
Cell Vol, L:	0.209	Tubing Vol,	0.072	System Vol, L:		0.2814	Leak Vol/min:	0.0000	Pass, <4%:	0.0152
Leak Check:	Initial, psia:	0.209	Time:	10:46		Final, psia:	0.218	Time: 12:21	Diff, atm,min:	0.009 / 95
Cell Vol, L:		Tubing Vol,	0.072	System Vol, L:		0.0724	Leak Vol/min:	0.0000	Pass, <4%:	0.0101

File Name(s)	Time (24hr)	Test Location	Sample Description	Flow (LPM)	Cell Pressure (atm)	Cell Temp (deg C)
BG1	10:31	1	Background House Nitrogen			
LAB2-	10:32	1	House Nitrogen			
BG2	11:09	1	Background House Nitrogen			
10mks5-9	12:19	2	ethylene 20 ppmV	4	0.94	150
bg10	12:28	1	background nitrogen	4	0.94	150
10mks11-21	12:31	1	nitrogen	4	0.94	150
10mks22-28	1:04	3	Petrifilm abatement inlet prestart	4	0.920	150
10mks29-111	13:12	3	Petrifilm abatement inlet run 1; temp ~360 F	4	0.920	150
10mks112-174	15:05	3	Petrifilm abatement inlet run 2; temp ~ 360 F	3	0.920	150
10mks175-290	16:09	3	Pre run 3 wanting to raise temp trouble	3	0.920	150
10mks291-367	18:05	3	Petrifilm abatement inlet run 3 raised temp on catalyst; ~ 390F	3	0.920	150
10mks368-370	19:23	1	Nitrogen purge	4	0.970	150
10mks371-375	19:29	2	ethylene 20 ppmV	4	0.970	150

Comments: Run 1 can pierced 13:31. Checked spectrum 65 MG2000 ~ 465 ppmV method analyzer JSE 440 ppmV, 5% diff DE ~ 98 % on runs 1 and 2 slightly higher. DE ~ 99.3 % on run 3.

3 EH&S Opns Environmental Laboratory				Extractive FTIR Sample Collection Data Sheet				Page 1 of 1		
Lab Req. No:	E18-0054	Baro, inHg:		0.00	psia	Signal 4K(cn		Signal 2K(cm^{-1}):		#DIV/0!
Project Name:	Brookings EtO Tests					Test Loc:	(1) nitrogen	CTS Cyl S.N.:	SG9169366BAL	
Computer ID:	9MKS	FTIR ID:	9MKS			(2)	ethylene 20 ppmV	(3)	test	
Operator (s):	KHS, JSE	Date:	1/30/2018			(4)	room air	(5)		
Ref. Method:	ETS-8.031	Quality Level:	(1) Screen	(2) Quantative	(3) Comp	(4) Validation				
Collection Dir:	9MKS_30Jan2018					Meth Nam		Inst. Res(cm^{-1}):	0.5	
# Scans, BG/Samp:	64	128	Time/Sample, min:	1.1	2.1	Sampling Interval:	0	Pathlength, m:	10	
Cells: PL,Vol	0.5cm, 0.0006	1cm, 0.0113	5cm, 0.0567	10cm, 0.113	4m, 0.209	10m, 2.13	Tape, 5.7	Parr, 0.636	Tube, ID in., length ft	0.0000
Leak Check:	Initial, psia:		Time:			Final, psia:		Time:	Diff, atm, min:	0 0
Cell Vol, L:		Tubing Vol,	0.000	System Vol, L:		0.0000	Leak Vol/min:	#DIV/0!	Pass, <4%:	#DIV/0!
Leak Check:	Initial, psia:		Time:			Final, psia:		Time:	Diff, atm,min:	0 0
Cell Vol, L:		Tubing Vol,	0.000	System Vol, L:		0.0000	Leak Vol/min:	#DIV/0!	Pass, <4%:	#DIV/0!

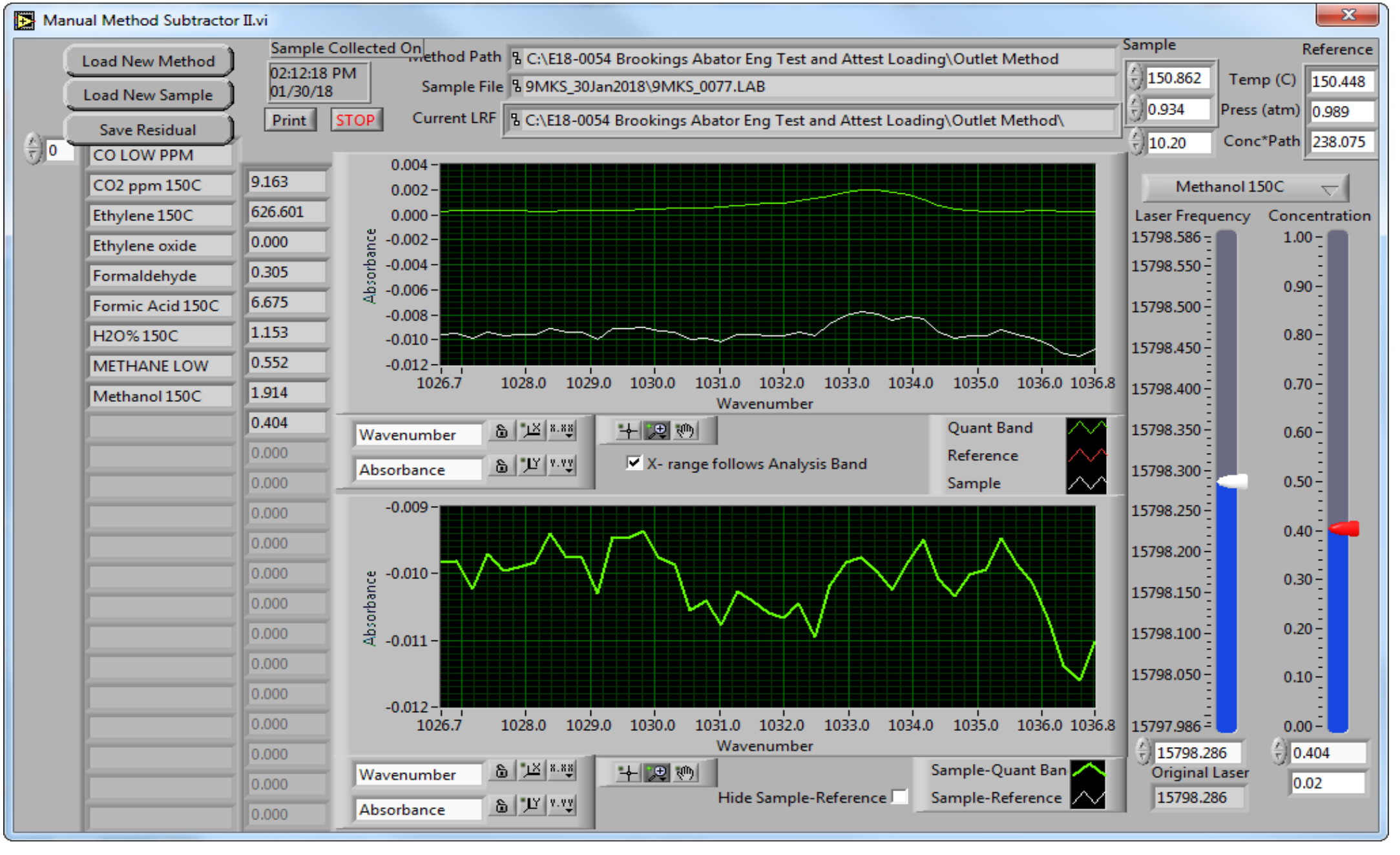
File Name(s)	Time (24hr)	Test Location	Sample Description	Flow (LPM)	Cell Pressure (atm)	Cell Temp (deg C)
BG1	11:18	1	Background Nitrogen			
LAB2-	11:20	1				
bg3	11:59	1	nitrogen background	2	0.94	150
9mks4-5	12:02	1	nitrogen sample	2	0.94	150
9mks6-12	12:13	2	ethylene 20 ppmV	4	0.94	150
9MKS13-	13:03	1	Sampling Petrifilm Abator Outlet	4		
	13:32		Run 1 Can Pierced			
	18:52		Flow lost			
9MKS355-359	19:22		20.0ppmV Ethylene	3		

Comments:

7.2 AutoQuant/MG2000 Methods

Spectrum 77 9mks Outlet results v7; kept tweaking method changing regions and adding compounds

	CO	CO2	Ethylene	EtO	Form	H2O	Methane	Methanol	Formic
MG2000	9.43	659.88	0.01	0.29	6.71	0.54	2.36	0.43	1.14
Manual	9.16	626.60	0.00	0.31	6.68	0.55	1.91	0.40	1.15
% diff	1.03	1.05	#DIV/0!	0.95	1.00	0.98	1.24	1.06	0.99
LOQ				0.28					



7.3 Pathlength Determination and Calibration Check

	Spectrum	Ethylene (ppmV)		
10mks_30Jan2018 Inlet	10MKS_0005.LAB	19.3		
	10MKS_0006.LAB	19.4		
	10MKS_0007.LAB	19.4	Cylinder Conc. (ppmV):	20.0
	10MKS_0008.LAB	19.4	Average (ppmV):	19.4
	10MKS_0009.LAB	19.4	Difference:	3.0%
10mks_30Jan2018 Inlet	10MKS_0371.LAB	19.3		
	10MKS_0372.LAB	19.4		
	10MKS_0373.LAB	19.4	Cylinder Conc. (ppmV):	20.0
	10MKS_0374.LAB	19.4	Average (ppmV):	19.4
	10MKS_0375.LAB	19.4	Difference:	3.2%
9mks_30Jan2018 Outlet	9MKS_0006.LAB	19.5		
	9MKS_0007.LAB	19.6		
	9MKS_0008.LAB	19.7		
	9MKS_0009.LAB	19.7		
	9MKS_0010.LAB	19.6	Cylinder Conc. (ppmV):	20.0
	9MKS_0011.LAB	19.6	Average (ppmV):	19.6
	9MKS_0012.LAB	19.4	Difference:	2.1%
9mks_30Jan2018 Outlet	9MKS_0355.LAB	19.5		
	9MKS_0356.LAB	19.5		
	9MKS_0357.LAB	19.5	Cylinder Conc. (ppmV):	20.0
	9MKS_0358.LAB	19.5	Average (ppmV):	19.5
	9MKS_0359.LAB	19.5	Difference:	2.4%

7.4 Calibration Gas Certification

Oxygen Service Company, Inc.

"An Employee Owned Company"
1111 PIERCE BUTLER RTE
ST. PAUL, MN 55104
(651)644-7273
FAX(651)644-2973

Certificate of Analysis

14901-67176
Product ID : 463

PURCHASE ORDER : 17-071 TK
CYLINDER # SG9169366BAL

COMPONENT	CAS NUMBER	REQUESTED CONCENTRATION	ACTUAL CONCENTRATION	UOM	ACCURACY +/-
		Mole	Mole		
ETHYLENE	74-85-1	20	20.0	ppm	1%
NITROGEN	7727-37-9	Balance	Balance	%	

METHOD OF ANALYSIS : GRAVIMETRIC & GAS CHROMATOGRAPHY
CYLINDER PRESSURE : 2015 PSIA
CYLINDER CONTENTS : 138 SCF
SHELF LIFE : 36 MONTHS
PRODUCED : 3/17/2017
EXPIRES : 3/17/2020

THIS MIXTURE WAS MADE TO A MINIMUM OF +/-1% ACCURACY USING SCALES THAT HAVE MONTHLY CARIBRATION CHECKS FOR PROCESS CONTROL PURPOSES. SCALES ARE CALIBRATED TWICE A YEAR BY "ALLOMETRICS" WITH N.I.S.T. WEIGHT SET ALLO1610 & ALLO049. THIS CALIBRATION PROCEDURE IS DEFINED IN MIL. STD 45662.

ANALYST

7.5 General Project Outline

3M EHS Laboratory General Project Outline

To: Paul Peterson – 3M Brookings
From: Jess Eldridge – 3M EHS Laboratory
CC: Brian Mader – 3M EHS Laboratory
Kelly Sater – 3M EHS Laboratory
Tim Gutzkow – 3M EHS Laboratory
Date: 1/17/2018
Subject: **3M Brookings Petri Film EtO Abator DE Engineering Test and Attest Lab Sterilizers EtO Emission – General Project Outline (GPO)**

➢ Project Objective:

The objective of this project is to conduct 2 different tests. The first test will be a destruction efficiency (DE) engineering test on the existing Petrifilm abatement. This test will provide information regarding the performance of the unit in advance of a compliance monitoring event scheduled in March 2018. The second test will be performed on the Attest Lab sterilizers combined exhaust to gather information on emission rates for the design of a future abatement unit.

Project Requested by:

Paul Peterson
3M Brookings Env Eng
Dept. Number: 104180
1-605-696-1445
p-peterson@mmm.com

Project Coordinated by:

Jess Eldridge
EHS Laboratory Analyst
1-651-733-9863
jseldridge@mmm.com

➢ Test and Reporting Summary

Test Location	3M Brookings SD
Process/Run Parameters	Petrifilm abatement inlet, outlet, 1 hour run time, number of runs to be determined. Inlet/outlet flow rates assumed equal no air flows measured, DE based on concentration. Attest exhaust concentration and flow. Flow measurements unsure of technique at time of writing of this document; possibly from sterilizers flow meters or tracer gas injection (SF6).
Sampling Parameters	FTIR based EtO concentrations, flow rates if feasible on Attest emission calculations
Target Analytes	Ethylene oxide, other compounds if present
Test Schedule	Travel/setup 1/29/18 Setup/test Petrifilm abatement 1/30/18 Setup/test Attest exhaust 1/30/18 Test/takedown Attest exhaust 1/31/18 if needed
Estimated Report Date	3/9/18
Report to:	Paul Peterson
Reporting Requirements	Detailed Report with supporting appendices
Report Classification	Confidential

➢ Safety

EHS Laboratory personnel will adhere to the stricter of the EHS Laboratory safety policy or the safety policy of the test location.

➢ Project Cost

Project Cost Recharge: $2,000.00
The requesting department will be re-charged this amount. The 3M Environmental Laboratory will cover all remaining project costs as a corporate operating expense.

Department Number for Re-charge: 104180

➢ Test Methods

1. Speciated FTIR Analysis – Modified EPA Method 320 (3M EL SOP ETS-08-31)

Assigned Project Quality Level: PQL2

The Environmental Laboratory maintains A2LA accreditation to ISO/IEC 17025 for the specific tests/calibrations as listed in A2LA Certificate #2052-01. The test results for FTIR analysis included in this project are NOT covered by this accreditation.